

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
31 October 2002 (31.10.2002)

PCT

(10) International Publication Number
WO 02/085788 A1

(51) International Patent Classification⁷: C01F 11/18, C01B 33/12, C04B 14/02, 26/26, 2/10, C08L 95/00

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.

(21) International Application Number: PCT/EP02/04336

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(22) International Filing Date: 18 April 2002 (18.04.2002)

(25) Filing Language: English

Published:

- with international search report
- before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 02/085788 A1

(54) Title: PROCESS FOR MINERAL CARBONATION WITH CARBON DIOXIDE

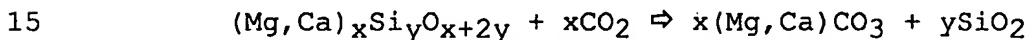
(57) Abstract: A process for mineral carbonation with carbon dioxide wherein carbon dioxide is reacted with a bivalent alkaline earth metal silicate, selected from the group of ortho-, di-, ring, and chain silicates, which silicate is immersed in an aqueous electrolytic solution. The invention further relates to the use of the mixture of carbonate and silica formed in such a process in construction materials and to the use of the carbonate formed by such a process for the production of calcium oxide.

PROCESS FOR MINERAL CARBONATION WITH CARBON DIOXIDE

The present invention relates to a process for mineral carbonation with carbon dioxide, to the use of the mixture of silica and carbonate formed in such a process in construction materials and to the use of the carbonate formed in such a process in the production of calcium oxide.

5 The rising of the carbon dioxide concentration in the atmosphere due to the increased use of energy derived from fossil fuels potentially has a large impact on 10 climate change. Measures to reduce the atmospheric carbon dioxide concentration are therefore needed.

In nature, stable mineral carbonate minerals and silica are formed by a reaction of carbon dioxide with natural silicate minerals:



The reaction in nature, however, proceeds at very low reaction rates.

Recently, the feasibility of such a reaction in 20 process plants has been studied. These studies mainly aim at increasing the reaction rate.

At the internet site of the US department of energy, <http://www.fetc.doe.gov/publications/factsheets/program/-prog006.pdf>, for example, is disclosed the reaction of finely ground serpentine ($\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$) or olivine (Mg_2SiO_4) in a solution of supercritical carbon dioxide and water to form magnesium carbonate. Under conditions of high temperature and pressure, 84% conversion of olivine has been achieved in 6 hours and a 80% conversion of pre-heated serpentine in less than an hour.

Other studies focus on the process of molten salt carbonation of mineral silicates with molten $MgCl_2$. This process is described by Walters et al. at the internet site [hppt:\www.netl.doe.gov/products/gcc/indepth/mineral/minarb.html](http://www.netl.doe.gov/products/gcc/indepth/mineral/minarb.html), and comprises the formation of magnesium hydroxide from magnesium silicates, via the formation of $MgCl_2$ using concentrated hydrochloric acid followed by hydrolysis of $MgCl_2$. Magnesium hydroxide is then carbonated in a direct gas solid reaction with carbon dioxide.

The above-mentioned processes, however, involve either the use of supercritical carbon dioxide or of concentrated hydrochloric acid. There is a need in the art for a rapid mineral carbonation process without the need of the use of supercritical conditions or of harmful or corrosive chemicals such as hydrochloric acid.

It has now been found that it is possible to react carbon dioxide with mineral silicates at an acceptable reaction rate if the reaction is performed with silicates that are immersed in an aqueous electrolyte solution.

Accordingly, the present invention relates to a process for mineral carbonation with carbon dioxide wherein carbon dioxide is reacted with a bivalent alkaline earth metal silicate, selected from the group of ortho-, di-, ring, and chain silicates, which silicate is immersed in an aqueous electrolyte solution.

In the process according to the invention, carbon dioxide is brought into contact with an aqueous electrolyte solution wherein the silicate is immersed. It will be appreciated that under such conditions, part of the carbon dioxide will dissolve in the aqueous solution and part will be present in the form of HCO_3^- or CO_3^{2-} ions.

5 Carbon dioxide may be brought into contact with the aqueous electrolyte solution wherein the silicate is immersed in any reactor suitable for gas-solid reactions in the presence of a liquid. Such reactors are known in the art. Examples of suitable reactors are a slurry bubble column or an extruder.

10 The ratio of mineral silicate to aqueous electrolyte solution depends inter alia on the type of reactor used, the particle size of the silica and process conditions like temperature and pressure.

15 In order to achieve a high reaction rate, it is preferred that the carbon dioxide concentration is high, which can be achieved by applying an elevated carbon dioxide pressure. Suitable carbon dioxide pressures are in the range of from 0.05 to 100 bar (absolute), preferably in the range of from 0.1 to 50 bar (absolute).

20 The total process pressure is preferably in the range of from 1 to 150 bar (absolute), more preferably of from 1 to 75 bar (absolute).

25 It is preferred that the silicate immersed in the electrolyte solution is in the form of small particles in order to achieve a high reaction rate. Particles having an average diameter of at most 5 mm may suitably be used. Preferably, the average diameter is at most 1 mm, more preferably at most 0.2 mm. Preferably, the average diameter is not smaller than 10 μm in order to avoid a very high energy input needed for particle size reduction.

30 Reference herein to the average diameter is to the volume medium diameter $D(v,0.5)$, meaning that 50 volume% of the particles have an equivalent spherical diameter that is smaller than the average diameter and 50 volume% of the particles have an equivalent spherical diameter that is greater than the average diameter. The equivalent

spherical diameter is the diameter calculated from volume determinations, e.g. by laser diffraction measurements.

It has been found that the reaction rate can be further increased when the silicate particles are reduced 5 in size during the process. This can be achieved by a process wherein the particles are mechanically broken up into smaller particles, for example by an extrusion, kneading or wet-milling process.

Alternatively, the process according to the invention 10 may be carried out by injecting carbon dioxide together with an aqueous electrolyte solution into underground layers that contain mineral silicates.

Suitable silicates for the process according to the invention are ortho-, di-, ring, and chain silicates.

15 Silicates are composed of orthosilicate monomers, i.e. the orthosilicate ion SiO_4^{4-} which has a tetrahedral structure. Orthosilicate monomers form oligomers by means of O-Si-O bonds at the polygon corners. The Q^s notation refers to the connectivity of the silicon atoms. The 20 value of superscript s defines the number of nearest neighbour silicon atoms to a given Si.

Orthosilicates, also referred to as nesosilicates, are silicates which are composed of distinct orthosilicate tetrathedra that are not bonded to each 25 other by means of O-Si-O bonds (Q^0 structure). An example of an orthosilicate is forsterite. Disilicates, also referred to as sorosilicates, have two orthosilicate tetrathedra linked to each other ($\text{Si}_2\text{O}_7^{6-}$ as unit structure, i.e. a Q^1Q^1 structure). Ring silicates, also 30 referred to as cyclosilicates, typically have SiO_3^{2-} as unit structure, i.e. a $(Q^2)_n$ structure. Chain silicates, also referred to as inosilicates, might be single chain

- 5 -

(SiO_3^{2-} as unit structure, i.e. a $(\text{Q}^2)_n$ structure) or double chain silicates ($(\text{Q}^3\text{Q}^2)_n$ structure).

5 Phyllosilicates, which are silicates having a sheet structure $(\text{Q}^3)_n$, and tectosilicates, which have a framework structure $(\text{Q}^4)_n$, are not suitable for the process according to the invention.

10 The silicates suitable for the process of the present invention are bivalent alkaline earth metal silicates, preferably calcium and/or magnesium silicates. Other metal ions, such as iron, aluminium, or manganese ions, may be present besides the bivalent alkaline earth metal ions. Especially in naturally-occurring silicates, both bivalent alkaline earth metal ions and other metal ions are present. An example is olivine which contains 15 bivalent iron ions and magnesium ions. Examples of calcium and/or magnesium silicates suitable for the process according to the invention are forsterite, olivine, monticellite, wollastonite, diopside, and enstatite.

20 The aqueous electrolyte solution in which the silicate is immersed is preferably a solution of a salt that has a solubility in water of at least 0.01 moles per litre at 298K and 1 atmosphere, preferably at least 0.1 moles per litre. Preferred salts are sodium, 25 potassium or barium salts, more preferably chlorides or nitrates of sodium, potassium or barium salts, i.e. NaCl , KCl , BaCl_2 , NaNO_3 , KNO_3 , or $\text{Ba}(\text{NO}_3)_2$, even more preferably sodium nitrate.

30 The electrolyte solution suitably has an electrolyte concentration of at least 0.01 moles/litres, preferably in the range of from 0.1 to 2 moles per litre.

The process according to the invention is preferably performed at elevated temperature. It will be appreciated

that the maximum temperature is determined by thermodynamic considerations. If calcium silicate is used, suitable temperatures are typically in the range of from 20 to 400 °C, preferably in the range of from 80 to 5 300 °C, more preferably of from 100 to 200 °C. If magnesium silicate is used, suitable temperatures are typically in the range of from 20 to 250 °C, preferably of from 100 to 200 °C.

10 The process according to the invention can suitably be used to remove carbon dioxide from natural gas. Thus, in a specific embodiment of the invention, carbon dioxide-containing natural gas is contacted with an aqueous electrolyte solution wherein silicate is immersed. If the natural gas is already available at 15 elevated pressure, there is no need to depressurise the gas before reacting it with silicate.

20 The mixture of carbonate and silica formed by the process of the invention can be disposed of, for example by refilling mining pits. It is, however, advantageous to form products from it having a commercial value.

25 In a further aspect of the invention, the mixture of carbonate and silica formed is used in construction materials. Examples of construction materials that can be produced from such a mixture are solid construction elements like building blocks, paving stones and roofing tiles composed of solid mineral particles and a binder as described in WO 00/46164. Such materials typically comprise from 70 to 99% by weight of solid particles and from 1 to 30% by weight of binder. These materials are 30 typically manufactured by mixing the solid particles with the molten binder and allowing the mixture to solidify. Suitable binders are commercially available. Hydrocarbonaceous binders such as described in WO 00/46164 are particularly suitable.

In a still further aspect, the invention relates to the use of the carbonate formed for the manufacture of calcium oxide. It is well-known to produce calcium oxide from carbonates. A disadvantage, however, of the manufacture of calcium oxide from carbonates obtained by mining is that the overall process is carbon dioxide producing. By using the carbonate formed in the carbonation process as hereinbefore described, the overall process is a carbon dioxide neutral process with respect to the stoichiometry of the reactions involved. In the manufacture of calcium oxide according to the invention, the carbonate may be used as a mixture with silica.

If carbonate and/or silica is separately desired, the products of the carbonation process of the invention can be separated by technologies known in the art, for example by density separation such as sink-flootation.

The process of the invention will be illustrated by means of the following examples.

20 EXAMPLE 1

Experiment 1 (according to the invention)

Wollastonite (CaSiO_3) powder having an average diameter ($D(v, 0.5)$) of 61 μm as measured by laser diffraction, was immersed in a solution of NaCl (0.04 g/ml) in water. The wollastonite concentration was 0.077 g/ml. The thus-obtained wollastonite slurry was brought, in a stirred autoclave, to a temperature of 180 °C and a pressure of 40 bar g. Carbon dioxide in an amount such that the pressure remained constant was continuously fed to the autoclave. Conversion was determined after one hour and after 3 hours reaction time by taking a sample of the slurry and measuring the weight loss after heating the dry reaction product at 900 °C and comparing the

weight loss to the theoretic maximum loss that would be achieved at 100% conversion.

Experiment 2 (comparative)

5 An experiment similar to experiment 1 was performed, but without NaCl in the wollastonite slurry.

EXAMPLE 2

Experiment 3 (according to the invention)

10 A slurry of 5 grams of fine wollastonite powder, having an average diameter ($D(v, 0.5)$) of 13 μm as measured by laser diffraction, in 50 ml of an aqueous NaCl solution (0.06 g/ml) was loaded into a glass flask. The slurry was brought to a temperature of 100 °C at ambient pressure. A mixture of nitrogen and carbon dioxide (50/50 v/v) was bubbled through the slurry at a 15 rate of 12 ml per minute. After 16 hours reaction time, the conversion was determined as described in experiment 1.

Experiment 4 (comparative)

20 An experiment similar to experiment 3 was performed, but without NaCl in the wollastonite slurry.

The results of the conversion measurements in experiments 1 to 4 are shown in the Table below.

TABLE

	NaCl conc. (moles/litre)	Conversion (%)		
		1h	3h	16h
Experiment 1	0.68	62	76	
Experiment 2	-	46	53	
Experiment 3	1.0			52
Experiment 4	-			22

C L A I M S

1. A process for mineral carbonation with carbon dioxide wherein carbon dioxide is reacted with a bivalent alkaline earth metal silicate, selected from the group of ortho-, di-, ring, and chain silicates, which silicate is
5 immersed in an aqueous electrolyte solution.
2. A process according to claim 1, wherein silicates particles are dispersed in the aqueous electrolyte solution.
3. A process according to claim 2, wherein the silicate
10 particles have an average diameter of at most 5 mm, preferably at most 1 mm, more preferably at most 0.2 mm.
4. A process according to claim 2 or 3, wherein the silicate particles are mechanically treated such that their size is reduced during the process.
- 15 5. A process according to claim 4, which is an extrusion process.
6. A process according to any one of the preceding claims, wherein the electrolyte is a salt having a solubility in water of at least 0.01 moles per litre,
20 preferably at least 0.1 moles per litre.
7. A process according to claim 6, wherein the electrolyte is a sodium, potassium or barium salt, more a chloride or nitrate of sodium, potassium or barium, even more preferably sodium nitrate.
- 25 8. A process according to any one of the preceding claims, wherein the concentration of electrolyte in the electrolyte solution is at least 0.01 moles per litre, preferably in the range of from 0.1 to 2 moles per litre.
9. A process according to any one of the preceding
30 claims, wherein the bivalent alkaline earth metal silicate is a magnesium or calcium silicate.

10. A process according to claim 9, wherein the silicate is a calcium silicate and the operating temperature is in the range of from 20 to 400 °C, preferably of from 80 to 300 °C, more preferably of from 100 to 200 °C.
- 5 11. A process according to claim 9, wherein the silicate is a magnesium silicate and the operating temperature is in the range of from 20 to 250 °C, preferably of from 100 to 200 °C.
- 10 12. A process according to any one of the preceding claims, wherein the operating pressure is in the range of from 1 to 150 bar (absolute), preferably of from 1 to 75 bar (absolute).
- 15 13. Use of the mixture of silica and carbonate formed by the process according of any one of the preceding claims in construction materials.
14. A process according to any one of claims 1 to 12 further comprising mixing the mixture of silica and carbonate formed with a molten binder and solidifying the silica/carbonate/binder mixture a construction material.
- 20 15. A process according to claim 14, wherein the binder is a hydrocarbonaceous binder.
16. Use of the carbonate formed by the process according of any one of claims 1 to 12 for the production of calcium oxide.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/04336

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C01F11/18 C01B33/12 C04B14/02 C04B26/26 C04B2/10
C08L95/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C01F C01B C04B C08L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

WPI Data, PAJ, EPO-Internal, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 00 46149 A (GRONCHI PAOLO ;CASSAR LUIGI (IT); ITALCEMENTI SPA (IT); MARCO TIZI) 10 August 2000 (2000-08-10) page 9, paragraph 2 claims 1-16 ---	13-15
A	US 1 697 722 A (CAMILLE DEGUIDE) 1 January 1929 (1929-01-01) the whole document ---	1-12
X	US 4 230 765 A (TAKIKAWA TORU ET AL) 28 October 1980 (1980-10-28) examples ---	13-16
A	---	1-12
	---	-/-

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the International filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the International filing date but later than the priority date claimed

- *T* later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *&* document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the International search report

3 September 2002

11/09/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patenttaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl.
Fax: (+31-70) 340-3016

Authorized officer

Zalm, W

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/04336

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>DATABASE WPI Section Ch, Week 197651 Derwent Publications Ltd., London, GB; Class L02, AN 1976-94982X XP002177996 & JP 51 125414 A (OSAKA PACKING SEIZOSHO KK), 1 November 1976 (1976-11-01) abstract</p> <p>---</p>	
A	<p>"Mineral Carbonation Study Program" date: 07/2000 'Online! Retrieval from Internet http://www.fetc.doe.gov/publications/factsheets/program/prog006.pdf Retrieval date: 20.9.2001 XP002177995 cited in the application the whole document</p> <p>---</p>	1-16
A	<p>WO 00 46164 A (REYNHOUT MARINUS JOHANNES ;SHELL INT RESEARCH (NL)) 10 August 2000 (2000-08-10) cited in the application the whole document</p> <p>---</p>	13-15

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/04336

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
WO 0046149	A	10-08-2000	IT	MI990197 A1		03-08-2000
			AU	2800100 A		25-08-2000
			WO	0046149 A1		10-08-2000
			EP	1149047 A1		31-10-2001
US 1697722	A	01-01-1929		NONE		
US 4230765	A	28-10-1980	JP	1106213 C		30-07-1982
			JP	51125699 A		02-11-1976
			JP	55014809 B		18-04-1980
			JP	1126024 C		14-12-1982
			JP	52008023 A		21-01-1977
			JP	55023788 B		25-06-1980
			JP	1128121 C		24-12-1982
			JP	52008024 A		21-01-1977
			JP	55023789 B		25-06-1980
			AU	502847 B2		09-08-1979
			AU	1229376 A		13-10-1977
			CA	1097030 A1		10-03-1981
			CA	1122778 A2		04-05-1982
			CA	1122779 A2		04-05-1982
			CA	1123172 A2		11-05-1982
			CA	1122780 A2		04-05-1982
			DE	2612281 A1		20-01-1977
			FR	2313315 A1		31-12-1976
			FR	2332955 A1		24-06-1977
			GB	1511125 A		17-05-1978
			IT	1058526 B		10-05-1982
			NL	7603156 A ,B,		28-09-1976
			SE	420596 B		19-10-1981
			SE	7603441 A		26-09-1976
			SE	7908472 A		12-10-1979
			US	4330519 A		18-05-1982
JP 51125414	A	01-11-1976	JP	1035099 C		26-02-1981
			JP	55023787 B		25-06-1980
WO 0046164	A	10-08-2000	AU	3151300 A		25-08-2000
			BR	0007942 A		06-11-2001
			CN	1342134 T		27-03-2002
			WO	0046164 A1		10-08-2000
			EP	1147068 A1		24-10-2001
			NO	20013652 A		01-10-2001
			TR	200102204 T2		21-05-2002